A Checking the validity of the $q = q^*$ approximation

All the results presented in this work for higher order correlations (e.g. the calculation of phase diagrams or critical points) use the $q = q^*$ approximation. This means that for the higher order vertex functions no explicit minimization over the q-parameter is performed, but instead the value of q is used where the second order vertex function attains its minimum ($q = q^*$ by definition). The validity of this approximation, which is also used in literature, has to be verified.

For a general binary system the free energy expression upto fourth order terms in the amplitude ψ and for a given set of external parameters [30] is given by:

$$F = (\Gamma_2(n,q) - 2\chi)\psi^2 - \gamma_3(n,q)\psi^3 + \gamma_4(n,q)\psi^4 \tag{219}$$

This free energy must be minimized with respect to the amplitude ψ, the inverse lengthscale q, and the symmetry of the structure n. The symmetry is labeled by a discrete variable $n = \{0,1,3,6\}$ which denotes the number of independent lattice vectors of the symmetry. The free energy of all the possible symmetries can be calculated and the smallest of these is selected to be the "minimal".

The problems arise in the minimization with respect to q and ψ. This minimization will lead to two equations which must be solved simultaneously.

$$\frac{\partial F}{\partial q} = 0 \quad \Rightarrow \quad \frac{\mathrm{d}\Gamma_2}{\mathrm{d}q} - \frac{\mathrm{d}\gamma_3}{\mathrm{d}q}\psi + \frac{\mathrm{d}\gamma_4}{\mathrm{d}q}\psi^2 = 0 \tag{220}$$

$$\frac{\partial F}{\partial \psi} = 0 \quad \Rightarrow \quad 2(\Gamma_2 - 2\chi) - 3\gamma_3\psi + 4\gamma_4\psi^2 = 0 \tag{221}$$

In (220) and (221) the trivial solution $\psi = 0$ has been removed.

A way to solve this system is by iteration. The value of the variable ψ is assumed to be small (this is the essence of weak segregation theory), therefore as a first guess we can set $\psi = 0$ and substitute this into Eq (220). This will give

$$\frac{\mathrm{d}\Gamma_2}{\mathrm{d}q} = 0 \quad \Rightarrow \quad q = q^* \tag{222}$$

This value of q is substituted into Eq (221) and a simple quadratic equation for ψ is obtained which will have a solution $\psi = \psi^*$.

These results q^* and ψ^* are normally used to calculate the free energy, but this set of variables is not the true minimum of the free energy. For instance if $\psi^* \neq 0$ then $q = q^*$ is no longer a solution of Eq (220). What needs to be verified is that further iteration of Eqs (220) and (221) leads to only small corrections in q and ψ.

[30] External parameters are for instance the overall composition, the architecture of the polymer, the chemical nature of the monomers, etc

To obtain information about the magnitude of this iteration correction, we will perform a leading order expansion in ψ, which is assumed to be small. From Eq (219) one can conclude that in the minimum all terms in this expression must have the same scaling behavior with respect to ψ. This means

$$\Gamma_2 - 2\chi \quad \propto \quad \psi^2 \tag{223}$$

$$\gamma_3 \propto \psi \tag{224}$$

What is also important is the fact that $\frac{d\gamma_3}{dq} \propto \psi$.

If a second iteration of Eqs (220) and (221) is performed, the variable $\psi = \psi^*$ is substituted into (220). Introducing $q = q^* + \delta q$, this will lead to the following expression upto leading order terms ($o(\psi^2)$)

$$\frac{d^2\Gamma_2^*}{dq^2}\delta q - \frac{d\gamma_3^*}{dq}\psi^* + \frac{d\gamma_4^*}{dq}(\psi^*)^2 = 0 \tag{225}$$

where $\gamma_3^* = \gamma_3(q = q^*)$, etc.

From this it follows $\delta q \propto \psi^2$ and therefore the correction on q [31] is small.

Substituting this new value for $q = q^* + \delta q$ into Eq (221) and using $\psi = \psi^* + \delta\psi$ will give upto leading order terms ($o(\psi^4)$)

$$-3\gamma_3^*\delta\psi + 8\gamma_4^*\psi^*\delta\psi + \frac{d^2\Gamma_2^*}{dq^2}(\delta q)^2 - 3\frac{d\gamma_3^*}{dq}\delta q\psi^* = 0 \tag{226}$$

Therefore it is shown that $\delta\psi \propto \psi^3$.[32] Thus for small ψ, the iterative corrections to it will be small.

We now can investigate the influence of the found corrections on the free energy expansion (219). The only correction upto fourth order in ψ is the correction $\frac{d\Gamma_2^*}{dq}\delta q(\psi^*)^2$, but this is zero by definition (222). Therefore it is concluded that taking into account corrections to the values of q^* and ψ^* will only give contributions to the free energy of higher order than 4 in ψ, which were already not taken into account. So upto fourth order in ψ the corrections play no role.

[31] The quantity q^* is normally of order 1, except for cases like random copolymers [11] where $q^* = 0$ and the correction terms are dominant.

[32] This only holds if $\psi^* \neq \frac{3\gamma_3^*}{8\gamma_4^*}$. If the inequality is not true, then expansions upto higher order must be investigated.

B Analytical solution of constant flow semibatch homopolymerization

The main results of this section are to be published in *Macromolecules* [60].

For the case of homopolymerization and constant flow an analytical treatment can be given for the monomer concentration and the average chain length.

For homopolymerization the kinetic equations (21) become much easier:

$$\frac{\mathrm{d}(VM)}{\mathrm{d}t} = -kRMV + qM^{\mathrm{in}} \tag{227}$$

If we assume a constant flow q with constant concentration M^{in}, we can write:

$$V(t) = V^0 + qt \tag{228}$$

Substitution of Eq (228) into Eq (227) gives:

$$\begin{aligned} \frac{\mathrm{d}M}{\mathrm{d}t} &= -kRM + \frac{q}{V}\left(M^{\mathrm{in}} - M\right) \\ &= -k\frac{V^0R^0}{V^0+qt}M + \frac{q}{V^0+qt}\left(M^{\mathrm{in}} - M\right) \\ &= -\frac{kV^0R^0+q}{V^0+qt}M + \frac{qM^{\mathrm{in}}}{V^0+qt} \end{aligned} \tag{229}$$

This inhomogeneous linear first order differential equation can be solved quite easily by using the method of "variation of paramters" on the homogeneous solution ($M^{\mathrm{in}} = 0$). The homogeneous solution is given by[33]:

$$M^h(t) = C(V^0+qt)^{-\frac{kV^0r^0+q}{q}} \tag{230}$$

where the constant C is determined by the initial condition $M(0) = M^0$. Applying the method of "variation of parameters" (by stating the constant C to be a function of time $C(t)$) leads to a differential equation for C:

$$\frac{\mathrm{d}C}{\mathrm{d}t} = qM^{\mathrm{in}}(V^0+qt)^{\frac{kV^0R^0}{q}} \tag{231}$$

This equation has the solution

$$C(t) = M^{\mathrm{in}}\frac{q}{kV_0R_0+q}(V_o+qt)^{\frac{kV^0R^0+q}{q}} + D \tag{232}$$

[33]Note that q is assumed to be nonzero. For $q = 0$ the system degenerates into a simple closed system.

where the constant of integration D is again determined by the initial conditions. Substition of Eq (231) into Eq (230) and expressing the constant D in terms of the initial concentration M^0 gives:

$$M(t) = M^{\text{in}}\frac{q}{kV^0R^0+q} + \left(M^0 - M^{\text{in}}\frac{q}{kV^0R^0+q}\right)\left(\frac{V^0}{V^0+qt}\right)^{\frac{kV^0R^0+q}{q}} \tag{233}$$

Thus the concentration of free monomers will go to a constant value $M^{\text{in}}q/(kV^0R^0 + q)$ for infinite polymerization time.

Also of interest is the dependence of the average polymer length with time. The average polymer length is given by the ratio of the number of consumed monomers over the number of macro-ions (25). Substitution of Eq (228) gives:

$$\begin{aligned} l(t) &= \frac{V^0M^0 + \int_0^t M^{\text{in}}(t')q(t')\mathrm{d}t' - M(t)V(t)}{R^0V^0} \\ &= \frac{V^0M^0 + tM^{\text{in}}q - M(t)[V^0+qt]}{R^0V^0} \\ &= \frac{M^0}{R^0} + \frac{M^{\text{in}}q}{R^0}\left[\frac{kR^0t-1}{kV^0R^0+q}\right] - \frac{M^0 - M^{\text{in}}\frac{q}{kV^0R^0+q}}{R^0}\left(\frac{V^0}{V^0+qt}\right)^{\frac{kV^0R^0}{q}} \end{aligned} \tag{234}$$

At large values of polymerization time the growth rate goes to a constant value:

$$\frac{\mathrm{d}l}{\mathrm{d}t} \to \frac{kM^{\text{in}}q}{kV^0R^0+q} \tag{235}$$

This shows that for any feed ($q > 0$ and $M^{\text{in}} > 0$) the polymers will reach infinite chain length at infinite polymerization time and that for large enough polymerization time the monomer concentration and the growthrate will go to a constant (positive) value.

An other result which follows from the calculation of $\frac{\mathrm{d}l}{\mathrm{d}t}$ is (we can take a time dependent q and M^{in} in this case):

$$\begin{aligned} \frac{\mathrm{d}l}{\mathrm{d}t} &= \frac{M^{\text{in}}(t)q(t) - \frac{\mathrm{d}M}{\mathrm{d}t}V(t) - M(t)q(t)}{R^0V^0} \\ &= \frac{M^{\text{in}}(t)q(t) - \left[-\frac{kV^0R^0+q(t)}{V(t)}M(t) + \frac{q(t)M^{\text{in}}(t)}{V(t)}\right]V(t) - M(t)q(t)}{R^0V^0} \\ &= kM(t) \end{aligned} \tag{236}$$

where use has been made of

$$V(t) = V^0 + \int_0^t q(t')\mathrm{d}t' \;\Rightarrow\; \frac{\mathrm{d}V}{\mathrm{d}t} = q(t) \tag{237}$$

Thus we obtain that the average length of a polymer in a semi-batch polymerization experiment is given by:

$$l(t) = k \int_0^t M(t')\mathrm{d}t' \tag{238}$$

C Derivation of binary kinetics

The main results of this section are to be published in *Macromolecules* [60].

From the master equations (2) and (1) it can be derived for binary systems that

$$\rho_\alpha = \sum_l \rho_\alpha(l) = \frac{R_\alpha}{R_0} = \frac{x_\alpha B_\alpha}{k_{\alpha\alpha}} \left(\sum_{\beta=1} \frac{x_\beta B_\beta}{k_{\beta\beta}} \right)^{-1} \tag{239}$$

where the coefficients B_α for a binary system can be found by [48]

$$B_\alpha = 1/r_{\overline{\alpha}} = \frac{k_{\overline{\alpha}\alpha}}{k_{\overline{\alpha}\overline{\alpha}}} \tag{240}$$

where the notation $\overline{\alpha}$ means "not α":

$$\overline{\alpha} = \begin{cases} \text{B} & \text{if } \alpha\text{=A} \\ \text{A} & \text{if } \alpha\text{=B} \end{cases} \tag{241}$$

The conversion p is defined by the following relationship:

$$p = 1 - \frac{M(t)}{M_0} \tag{242}$$

which is equivalent to the fraction of initial monomers which have been consumed in the polymerization process. Differentiation with respect to time gives

$$\frac{\mathrm{d}p}{\mathrm{d}t} = -\frac{1}{M_0} \frac{\mathrm{d}M}{\mathrm{d}t} \tag{243}$$

Now note that $M = \sum_\alpha M_\alpha$ and thus substitution of eq. (2) summed over α gives

$$\frac{\mathrm{d}p}{\mathrm{d}t} = \frac{R_0}{M_0} \sum_\alpha \sum_\beta k_{\beta\alpha} \rho_\beta M_\alpha \tag{244}$$

Substitution of eq. (239) gives

$$\frac{\mathrm{d}p}{\mathrm{d}t} = \frac{R_0}{M_0 \sum_\gamma \frac{x_\gamma B_\gamma}{k_{\gamma\gamma}}} \sum_\alpha \sum_\beta k_{\beta\alpha} \frac{x_\beta B_\beta}{k_{\beta\beta}} M_\alpha \tag{245}$$

Substitution of eq. (240) gives

$$\begin{aligned} \frac{\mathrm{d}p}{\mathrm{d}t} &= \frac{R_0}{M_0 \sum_\gamma \frac{x_\gamma k_{\overline{\gamma}\gamma}}{k_{\gamma\gamma} k_{\overline{\gamma}\overline{\gamma}}}} \sum_\alpha \sum_\beta k_{\beta\alpha} \frac{x_\beta k_{\overline{\beta}\beta}}{k_{\beta\beta} k_{\overline{\beta}\overline{\beta}}} M_\alpha \\ &= \frac{R_0}{M_0 \sum_\gamma x_\gamma k_{\overline{\gamma}\gamma}} \sum_\alpha \sum_\beta k_{\beta\alpha} x_\beta k_{\overline{\beta}\beta} M_\alpha \end{aligned} \tag{246}$$

where use has been made of the fact that for a **binary** system $K_{\beta\beta}k_{\overline{\beta}\beta}$ does not depend on β and so can be divided out. This greatly simplifies the equations.

By using the identity $x_\alpha = \frac{M_\alpha}{(1-p)M_0}$ we can transform the equation into

$$\begin{aligned}\frac{\mathrm{d}p}{\mathrm{d}t} &= \frac{R_0(1-p)}{\sum_\gamma x_\gamma k_{\overline{\gamma}\gamma}} \sum_\alpha \sum_\beta k_{\beta\alpha} x_\beta k_{\overline{\beta}\beta} x_\alpha \\ &= R_0(1-p)\frac{\sum_\alpha x_\alpha k_{\overline{\alpha}\alpha} \sum_\beta k_{\alpha\beta} x_\beta}{\sum_\alpha x_\alpha k_{\overline{\alpha}\alpha}} \qquad (247) \\ &= R_0(1-p)F(x(p)) \qquad (248)\end{aligned}$$

We want to obtain equations for x_α, therefore we start from eq. (2)

$$\frac{\mathrm{d}M_\alpha(t)}{\mathrm{d}t} = -R_0 \sum_\beta k_{\beta\alpha}\rho_\beta(t) M_\alpha(t) \qquad (249)$$

Transformation to conversion space gives

$$\frac{\mathrm{d}M_\alpha(p)}{\mathrm{d}p} = -\frac{R_0}{\frac{\mathrm{d}p}{\mathrm{d}t}} \sum_\beta k_{\beta\alpha}\rho_\beta(p) M_\alpha(p) \qquad (250)$$

Substitution of eq. (247) and (239) gives

$$\frac{\mathrm{d}M_\alpha}{\mathrm{d}p} = \frac{-1}{1-p}\frac{\sum_\beta k_{\beta\alpha} x_\beta k_{\overline{\beta}\beta} M_\alpha}{\sum_\beta x_\beta k_{\overline{\beta}\beta} \sum_\gamma k_{\beta\gamma} x_\gamma} \qquad (251)$$

To check this rather cumbersome equation we can take a sum over α on both sides to obtain

$$\begin{aligned}\frac{\mathrm{d}M}{\mathrm{d}p} &= \frac{-1}{1-p}\frac{\sum_\alpha \sum_\beta k_{\beta\alpha} x_\beta k_{\overline{\beta}\beta} M_\alpha}{\sum_\beta x_\beta k_{\overline{\beta}\beta} \sum_\gamma k_{\beta\gamma} x_\gamma} \\ &= -M_0 \frac{\sum_\alpha \sum_\beta k_{\beta\alpha} x_\beta k_{\overline{\beta}\beta} x_\alpha}{\sum_\beta x_\beta k_{\overline{\beta}\beta} \sum_\gamma k_{\beta\gamma} x_\gamma} \\ &= -M_0 \qquad (252)\end{aligned}$$

which was to be expected from eq (242).

We can substitute $M_\alpha = M x_\alpha$ into eq (251)

$$\begin{aligned}\frac{\mathrm{d}M x_\alpha}{\mathrm{d}p} &= \frac{-1}{1-p}\frac{\sum_\beta k_{\beta\alpha} x_\beta k_{\overline{\beta}\beta} M x_\alpha}{\sum_\beta x_\beta k_{\overline{\beta}\beta} \sum_\gamma k_{\beta\gamma} x_\gamma} \\ \frac{\mathrm{d}M}{\mathrm{d}p} x_\alpha + M\frac{\mathrm{d}x_\alpha}{\mathrm{d}p} &= \frac{-M}{1-p}\frac{\sum_\beta k_{\beta\alpha} x_\beta k_{\overline{\beta}\beta} x_\alpha}{\sum_\beta x_\beta k_{\overline{\beta}\beta} \sum_\gamma k_{\beta\gamma} x_\gamma}\end{aligned}$$

$$\begin{aligned}
\frac{\mathrm{d}x_\alpha}{\mathrm{d}p} &= \frac{M_0}{M}x_\alpha - \frac{1}{1-p}\frac{\sum_\beta k_{\beta\alpha}x_\beta k_{\bar\beta\beta}x_\alpha}{\sum_\beta x_\beta k_{\bar\beta\beta}\sum_\gamma k_{\beta\gamma}x_\gamma} \\
&= \frac{1}{1-p}\left[x_\alpha - \frac{\sum_\beta k_{\beta\alpha}x_\beta k_{\bar\beta\beta}x_\alpha}{\sum_\beta x_\beta k_{\bar\beta\beta}\sum_\gamma k_{\beta\gamma}x_\gamma}\right] \\
&= \frac{1}{1-p}\left[x_\alpha - Y_\alpha\right] \qquad (253)
\end{aligned}$$

The equation looks in form the same as eq (13), we only need to prove that $Y_A = \pi_A$.

$$\begin{aligned}
\pi_\alpha &= \frac{x_\alpha(r_\alpha x_\alpha + x_{\bar\alpha})}{r_\alpha x_\alpha^2 + r_{\bar\alpha}x_{\bar\alpha}^2 + 2x_\alpha x_{\bar\alpha}} \\
&= \frac{k_{\bar\alpha\alpha}x_\alpha(k_{\alpha\alpha}x_\alpha + k_{\alpha\bar\alpha}x_{\bar\alpha})}{k_{\bar\alpha\alpha}k_{\alpha\alpha}x_\alpha^2 + k_{\alpha\bar\alpha}k_{\bar\alpha\bar\alpha}x_{\bar\alpha}^2 + 2k_{\bar\alpha\alpha}k_{\alpha\bar\alpha}x_\alpha x_{\bar\alpha}} \\
&= \frac{k_{\alpha\alpha}k_{\bar\alpha\alpha}x_\alpha^2 + k_{\alpha\bar\alpha}k_{\bar\alpha\alpha}x_\alpha x_{\bar\alpha}}{k_{\bar\alpha\alpha}k_{\alpha\alpha}x_\alpha^2 + k_{\alpha\bar\alpha}k_{\bar\alpha\bar\alpha}x_{\bar\alpha}^2 + 2k_{\bar\alpha\alpha}k_{\alpha\bar\alpha}x_\alpha x_{\bar\alpha}} \\
Y_\alpha &= \frac{\sum_\beta k_{\beta\alpha}x_\beta k_{\bar\beta\beta}x_\alpha}{\sum_\beta x_\beta k_{\bar\beta\beta}\sum_\gamma k_{\beta\gamma}x_\gamma} \\
&= \frac{k_{\alpha\alpha}x_\alpha k_{\bar\alpha\alpha}x_\alpha + k_{\bar\alpha\alpha}x_{\bar\alpha}k_{\alpha\bar\alpha}x_\alpha}{x_\alpha k_{\bar\alpha\alpha}(k_{\alpha\alpha}x_\alpha + k_{\alpha\bar\alpha}x_{\bar\alpha}) + x_{\bar\alpha}k_{\alpha\bar\alpha}(k_{\bar\alpha\alpha}x_\alpha + k_{\bar\alpha\bar\alpha}x_{\bar\alpha})} \\
&= \frac{k_{\alpha\alpha}k_{\bar\alpha\alpha}x_\alpha^2 + k_{\bar\alpha\alpha}k_{\alpha\bar\alpha}x_\alpha x_{\bar\alpha}}{x_\alpha^2 k_{\bar\alpha\alpha}k_{\alpha\alpha} + 2x_\alpha x_{\bar\alpha}k_{\alpha\bar\alpha}k_{\bar\alpha\alpha} + x_{\bar\alpha}^2 k_{\alpha\bar\alpha}k_{\bar\alpha\bar\alpha}} \qquad (254)
\end{aligned}$$

Thus $Y_\alpha = \pi_\alpha$.

Equation (13) can be solved easily by explicit integration

$$\frac{\mathrm{d}x}{\mathrm{d}p} = \frac{x - \pi_A(x)}{1-p} \qquad (255)$$

becomes

$$\begin{aligned}
\frac{\mathrm{d}p}{1-p} &= \frac{\mathrm{d}x}{x - \pi_A(x)} \\
\ln|1-p| &= \int \frac{\mathrm{d}x}{x - \pi_A(x)} \qquad (256)
\end{aligned}$$

which after a little work will give the solution (14).

D Scattering in multicomponent systems

The main results of this section are to be published in *Macromolecules* [60].

The scattering intensity I of an n-component system at an angle θ with respect to the incident radiation with wave length λ can be calculated by the expression [95]

$$I(q) = \sum_{\alpha}\sum_{\beta} a_\alpha a_\beta \widetilde{S}_{\alpha\beta}(q), \qquad \text{where } q = \frac{4\pi}{\lambda}\sin\frac{\theta}{2} \tag{257}$$

where a_α is the scattering length of an α-th type monomeric units. In view of the spatial isotropy of the system the Fourier component $\widetilde{S}_{\alpha\beta}(q)$ of elements $S_{\alpha\beta}(\mathbf{r})$ of the correlation matrix and, consequently, the scattering intensity will depend only on the modulus q of the wave vector $\mathbf{q}$. For incompressible systems the expression (257) is written down in the following manner

$$I(q) = -\sum_{\alpha<\beta} \left(a_\alpha - a_\beta\right)^2 \widetilde{S}_{\alpha\beta}(q) \tag{258}$$

where the structural matrix $\widetilde{\mathbf{S}}(q)$ may be presented as [35]

$$\widetilde{\mathbf{S}}(q) = \rho\left[\mathbf{b} - \mathbf{b}\left(\widetilde{\mathbf{X}} + \mathbf{b}\right)^{-1}\mathbf{b}\right] \tag{259}$$

Apart from the overall density of monomeric units ρ two matrices enter into the right-hand side of this formula. One of them, $\mathbf{b}$, describes the pair interactions of monomeric units. Its elements are in a simple manner connected with the elements of matrix $\mathbf{d}$ inverse to matrix χ of the Flory-Huggins parameters

$$b_{\alpha\beta} = d_{\alpha\beta} - \sum_{\beta} d_{\alpha\beta}\sum_{\alpha} d_{\alpha\beta}\left(\sum_{\alpha}\sum_{\beta} d_{\alpha\beta}\right)^{-1} \tag{260}$$

with

$$\mathbf{d} = \begin{pmatrix} \chi_{11} & \cdots & \chi_{1n} \\ \vdots & \ddots & \vdots \\ \chi_{n1} & \cdots & \chi_{nn} \end{pmatrix}^{-1} \tag{261}$$

The second matrix, $\widetilde{\mathbf{X}}$, equal up to a factor ρ to the structure matrix $\widetilde{\kappa}(q)$, is expressed through the generating functions of two-point chemical correlators $W_{\alpha\beta}(x)$

$$\begin{aligned} \widetilde{X}_{\alpha\beta}(q) &\equiv \widetilde{\kappa}_{\alpha\beta}(q)/\rho = X_\alpha\delta_{\alpha\beta} + W_{\alpha\beta}(x) + W_{\beta\alpha}(x), \\ x &= e^{-Q} \qquad\qquad Q = a^2q^2/6 \end{aligned} \tag{262}$$

where a represents the size of a monomeric unit. Thus, equations (257)-(262) jointly with the expression (111) provide an exact solution of the problem of determining the

scattering function of melt of a copolymer obtained by "living" anionic copolymerization of an arbitrary number of monomer types.

The amplitude of scattering (257) becomes infinite at the spinodal where the spatially-homogeneous state of a polymer liquid turns out to be absolutely unstable with respect to composition fluctuations. Such a stability loss may happen either at the zero wave vector ($q^* = 0$) or at a non-zero wave vector ($q^* \neq 0$). These two cases are referred to as the trivial and nontrivial spinodal branches, respectively. The trivial branch is described by the condition of vanishing of the determinant $D\left(q^2\right)$ of the matrix $\widetilde{\mathbf{X}}(q) + \mathbf{b}$ at $q = 0$

$$D(0) = 0 \tag{263}$$

To find the nontrivial branch of the spinodal, where the zero $q = q^*$ of the function $D\left(q^2\right)$ is double degenerate, it is necessary to solve the set of two equations

$$D\left(q^2\right) = 0 \qquad \frac{dD\left(q^2\right)}{d\left(q^2\right)} = 0 \tag{264}$$

Within the framework of the integral approximation considered in Section 1 (long chain length approximation) the formulas for the calculation of the amplitude of scattering and the spinodal are substantially simplified because expression (262) is reducible in this case to the following form

$$\begin{aligned} \widetilde{X}_{\alpha\beta}(q) &= \frac{l_m}{p}\int_0^p dp' \int_0^{p'} dp'' X_\alpha\left(p'\right) X_\beta\left(p''\right) \exp\left\{-y\left|p' - p''\right|\right\}, \\ y &= Ql_m = q^2\overline{R_G^2} \text{where} R_G^2 = a^2 l_m/6 \end{aligned} \tag{265}$$

When calculating the spinodal it is convenient to introduce the variables

$$z_\alpha\left(p'; p\right) \equiv X_\alpha\left(p'\right) - \langle X_\alpha \rangle \tag{266}$$

describing the diffrence between the conditional probability $X_\alpha(i) = P_\alpha(i)$ to find a unit of type α, located at $i = l_m p'$ distance from the beginning of the chain, from the unconditional probability $\langle X_\alpha \rangle$ (8) to find such a unit at any place of a macromolecule. The functions z_α in Eq (266) determine the following integrals

$$I^{(0)}(y) \equiv \left\langle u^{(0)} \right\rangle_s, \quad I_\alpha^{(1)}(y) \equiv \left\langle u_\alpha^{(1)} \right\rangle_s \quad I_{\alpha\beta}^{(2)}(y) \equiv \left\langle u_{\alpha\beta}^{(2)} \right\rangle_s \tag{267}$$

where angular brackets with subscript $_s$ denote the effect of the integral operator

$$\left\langle u_{\alpha_1 \ldots \alpha_s}^{(s)} \right\rangle_s \equiv \frac{l_m}{p}\int_0^p dp' \int_0^{p'} dp'' u_{\alpha_1 \ldots \alpha_s}^{(s)} \exp\left\{-y\left|p' - p''\right|\right\} \tag{268}$$

on the functions

$$u^{(0)} = 1, \qquad u_\alpha^{(1)} = z_\alpha\left(p'; p\right), \qquad u_{\alpha\beta}^{(2)}\left(p', p''; p\right) = z_\alpha\left(p'; p\right) z_\beta\left(p''; p\right) \tag{269}$$

standing between the brackets.

We can write the matrix $\widetilde{\mathbf{X}}+\mathbf{b}$ elements in a more convenient form

$$\widetilde{X}_{\alpha\beta}+b_{\alpha\beta}=U_{\alpha\beta}+I^{(0)}\eta_{\alpha}\eta_{\beta} \tag{270}$$

where the following designations are used

$$\begin{aligned} U_{\alpha\beta} &\equiv \Delta_{\alpha\beta}+B_{\alpha\beta} \qquad \eta_{\alpha}\equiv\langle X_{\alpha}\rangle+\frac{I^{(1)}}{I^{(0)}} \\ \Delta_{\alpha\beta}(y) &\equiv I^{(2)}_{\alpha\beta}(y)-\frac{I^{(1)}_{\alpha}(y)\,I^{(1)}_{\beta}(y)}{I^{(0)}(y)} \end{aligned} \tag{271}$$

one can find this matrix determinant

$$D\left(q^2\right)=I^{(0)}(y)\,U(y) \tag{272}$$

which equals the product of positive integral $I^{(0)}(y)$ and any cofactor $U(y)$ of the matrix **U** with elements (271). Thus, the conditions (264) of finding of nontrivial spinodal branch will assume within the framework of the approximation of interest the following form

$$U(y)=0, \qquad \frac{dU(y)}{dy}=0 \tag{273}$$

where variable y is related to the wave vector q by the relationship (265).

In the case of binary copolymerization when

$$z_1=-z_2, \quad I^{(1)}\equiv I^{(1)}_1=-I^{(1)}_2, \quad I^{(2)}\equiv I^{(2)}_{11}=I^{(2)}_{22}=-I^{(2)}_{12} \tag{274}$$

the expression for the amplitude of scattering (257) will read

$$I(q) = (a_1-a_2)^2\,\frac{b\Delta(y)}{\Delta(y)+b} \tag{275}$$

$$\textit{where} \qquad \Delta(y) = I^{(2)}(y)-\frac{\left[I^{(1)}(y)\right]^2}{I^{(0)}(y)}, \qquad b=-\frac{1}{2\chi}$$

E Derivation of correlation functions for tapered Markov chains

In this appendix we will derive the exact expression for $\overline{\sigma_\alpha(i)\sigma_\beta(j)}$ for tapered Markovian copolymers.

We start by considering the Markov matrix (11) as a stochastic matrix [34] $\mathcal{M}(p)$ [35]. for given conversion p

The matrix $\mathcal{M}(p)$ has eigenvalues 1 and $\lambda(p)$ and two sets of eigenvectors; two right-eigenvectors $\left\{\vec{e}_1^R(p), \vec{e}_2^R(p)\right\}$ and two left-eigenvectors $\left\{\vec{e}_1^L(p), \vec{e}_2^L(p)\right\}$ which are defined by

$$\begin{cases} \mathcal{M}(p)\,\vec{e}_1^R(p) = \vec{e}_1^R(p) \\ \mathcal{M}(p)\,\vec{e}_2^R(p) = \lambda(p)\,\vec{e}_1^R(p) \end{cases}$$

and

$$\begin{cases} \vec{e}_1^L(p)\,\mathcal{M}(p) = \vec{e}_1^R(p) \\ \vec{e}_2^L(p)\,\mathcal{M}(p) = \lambda(p)\,\vec{e}_1^R(p) \end{cases}$$

with $\vec{e}_i^L(p)\cdot\vec{e}_j^R(p) = \delta_{ij}$.

We introduce two additional 2 by 2 matrices $\mathcal{R}(p)$ and $\mathcal{L}(p)$ given by

$$\mathcal{R}(p) = \begin{pmatrix} e_{11}^R(p) & e_{12}^R(p) \\ e_{21}^R(p) & e_{22}^R(p) \end{pmatrix}$$

and

$$\mathcal{L}(p) = \begin{pmatrix} e_{11}^L(p) & e_{12}^L(p) \\ e_{21}^L(p) & e_{22}^L(p) \end{pmatrix}$$

The following identities can be derived:

$$\mathcal{L}(p)\,\mathcal{M}(p)\,\mathcal{R}^T(p) = \mathcal{M}_d(p) \equiv \begin{pmatrix} 1 & 0 \\ 0 & \lambda(p) \end{pmatrix} \tag{276}$$

$$\mathcal{M}(p) = \mathcal{R}^T(p)\,\mathcal{M}_d(p)\,\mathcal{L}(p) \tag{277}$$

$$\mathcal{L}(p)\,\mathcal{R}^T(p) = I \equiv \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{278}$$

$$\mathcal{R}^T(p)\mathcal{L}(p) = \mathcal{G} \equiv \mathcal{G}_1 + \mathcal{G}_2 \tag{279}$$

where $\mathcal{G}$ is the metric tensor connected to a coordinate system spanned by the eigenvectors of $\mathcal{M}$.

The value of $\mathcal{G}$ can be calculated by considering the following transformation. The LHS (left-hand-side) of Eq. 280 are the base vectors of the Cartesian coordinate

[34] A stochastic matrix is a matrix of which all columns add up to unity and all elements are positive.

[35] Caligraphic letter will be used to denote 2 by 2 matrices.

suytem. The RHS of Eq. 280 are the right eigenvectors $\vec{e}_1^R$ and $\vec{e}_2^R$) of the Markov matrix $\mathcal{M}$.

$$\left(\begin{array}{c} 1 \\ 0 \end{array} \right), \left(\begin{array}{c} 0 \\ 1 \end{array} \right) \rightarrow \left(\begin{array}{c} 1 \\ -1 \end{array} \right), \left(\begin{array}{c} 1 \\ a \end{array} \right) \tag{280}$$

with $a = \frac{1-M_{AA}}{1-M_{BB}}$ and the elements of $\mathcal{G}$ are defined by

$$\mathcal{G}^{\mu\nu} = \frac{\partial m^i \partial m^j}{\partial n^\nu \partial n^\mu} g^{ij} \tag{281}$$

where m^i are the coefficients of the cartesian coordinate system (LHS of Eq. 280), and n^μ the coefficients of the new eigenbasis. The tensor g is the metric tensor of the cartesian coordinate system and it is equal to the identity matrix I. From this it follows

$$\mathcal{G}(p) = \left(\begin{array}{cc} 1+a^2 & 1-a \\ 1-a & 2 \end{array} \right) \tag{282}$$

We can rewrite $\mathcal{M}_d(p)$ as

$$\mathcal{M}_d(p) = \mathrm{e}^{\Lambda(p)} \text{ with } \Lambda(p) = \left(\begin{array}{cc} 0 & 0 \\ 0 & \ln\lambda(p) \end{array} \right)$$

Thus

$$\begin{aligned} \mathcal{M}(p) &= \mathcal{R}^T(p)\, \mathrm{e}^{\Lambda(p)}\, \mathcal{L}(p) \\ &= \sum_{n=0}^{\infty} \frac{1}{n!} \mathcal{R}^T(p) \Lambda(p)^n \mathcal{L}(p) \\ &= \sum_{n=0}^{\infty} \frac{1}{n!} \left[\mathcal{R}^T(p) \Lambda(p) \mathcal{L}(p) \right]^n \\ &= \exp\left[\mathcal{R}^T(p) \Lambda(p) \mathcal{L}(p) \right] \end{aligned}$$

and

$$\begin{aligned} \mathcal{R}^T(p) \Lambda(p) \mathcal{L}(p) &= \left(\begin{array}{cc} e_{11}^R & e_{21}^R \\ e_{12}^R & e_{22}^R \end{array} \right) \left(\begin{array}{cc} 0 & 0 \\ 0 & \ln\lambda(p) \end{array} \right) \left(\begin{array}{cc} e_{11}^L & e_{12}^L \\ e_{21}^L & e_{22}^L \end{array} \right) \\ &= \left(\begin{array}{cc} e_{21}^R e_{21}^L & e_{21}^R e_{22}^L \\ e_{22}^R e_{21}^L & e_{22}^R e_{22}^L \end{array} \right) \ln\lambda(p) \equiv \mathcal{G}_2(p) \ln\lambda(p) \end{aligned}$$

and thus

$$\mathcal{M}(p) = \exp\left[\mathcal{G}_2(p) \ln\lambda(p) \right] \tag{283}$$

We now consider $\overline{\sigma_\alpha(i)\sigma_\beta(j)}$ with $j > i$. We can rewrite this as

$$\overline{\sigma_\alpha(i)\sigma_\beta(j)} = \overline{\sigma}_\alpha(i) \left\{ \prod_{l=1}^{j-i} \mathcal{M}\left(\frac{i+l}{N} \right) \right\}_{\alpha\beta}$$

$$= \overline{\sigma}_\alpha(i) \exp\left[\sum_{l=1}^{j-i} \mathcal{G}_2\left(\frac{i+l}{N}\right) \ln\lambda\left(\frac{i+l}{N}\right)\right] \quad (284)$$

$$\approx \overline{\sigma}_\alpha(pN) \exp\left[N \int_{i/N}^{j/N} \mathrm{d}p' \mathcal{G}_2\left(p'\right) \ln\lambda\left(p'\right)\right] \quad (N \gg 1) \quad (285)$$

F Derivation of distribution functions for diblock copolymer destruction

This section was published as appendix to [79]

When solving Eqs (164)-(166), let us take advantage of the fact that the independence of MWDs of the blocks of the initial copolymer molecules is retained during the degradation. Due to this important property, the concentration of block copolymer molecules at any moment of time admits the factorization

$$C_{12}(l_1, l_2) = Y^0 f_1(l_1) f_2(l_2) \tag{286}$$

The evolution of the MWD of α-th type blocks, $f_\alpha(l_\alpha)$, is described by the solution of the following equation

$$\frac{1}{k_\alpha}\frac{\mathrm{d}f_\alpha(l_\alpha)}{\mathrm{d}t} = \int_{l_\alpha}^{\infty} f_\alpha(\xi)\,d\xi - l_\alpha f_\alpha(l_\alpha) \quad (\alpha = 1,2) \tag{287}$$

where the function $f_\alpha(l_\alpha)$ at moment $t = 0$ is $f_\alpha^0(l_\alpha)$. Distributions $f_1(l_1)$ and $f_2(l_2)$ found in such a way will occur in the right-hand part of eqs (3) and (4), which being substituted into expression (286), will read

$$\frac{1}{k_\alpha}\frac{\mathrm{d}C_\alpha(l_\alpha)}{\mathrm{d}t} = Y^0 \int_{l_\alpha}^{\infty} f_\alpha(\xi)\,d\xi + 2\int_{l_\alpha}^{\infty} C_\alpha(\xi)\,d\xi - l_\alpha C_\alpha(l_\alpha) \quad (\alpha = 1,2) \tag{288}$$

To solve the integro-differential equations (Eqs (287) and (288)) it is convenient to go from functions $f_\alpha(l_\alpha)$ and $C_\alpha(l_\alpha)$ to their Laplace transforms

$$\begin{aligned} g_\alpha(p_\alpha) &\equiv \widetilde{f}_\alpha(p_\alpha) = \int_0^{\infty} f_\alpha(l_\alpha)\exp(-p_\alpha l_\alpha)\,dl_\alpha \\ \widetilde{C}_\alpha(p_\alpha) &= \int_0^{\infty} C_\alpha(l_\alpha)\exp(-p_\alpha l_\alpha)\,dl_\alpha \end{aligned} \tag{289}$$

in terms of which Eqs (287) and (288) will turn into

$$\frac{1}{k_\alpha}\frac{\partial g_\alpha(p_\alpha)}{\partial t} = \frac{1}{p_\alpha}\left[g_\alpha(0) - g_\alpha(p_\alpha)\right] + \frac{\partial g_\alpha(p_\alpha)}{\partial p_\alpha} \tag{290}$$

$$\frac{1}{k_\alpha}\frac{\partial \widetilde{C}_\alpha(p_\alpha)}{\partial t} = \frac{Y^0}{p_\alpha}\left[g_\alpha(0) - g_\alpha(p_\alpha)\right] + \frac{2}{p_\alpha}\left[\widetilde{C}_\alpha(0) - \widetilde{C}_\alpha(p_\alpha)\right] + \frac{\partial \widetilde{C}_\alpha(p_\alpha)}{\partial p_\alpha} \quad (291)$$

In order to find the unknown functions $g_\alpha(0)$ and $\widetilde{C}_\alpha(0)$ involved in the above equations, a transition to the limit $p_\alpha \to 0$ should be carried out in their right-hand parts. As a result we will get 0 and X_α for Eq (290) and Eq (291), respectively, which with allowance for initial conditions $g^0_\alpha(0) = 1$ and $\widetilde{C}^0_\alpha(0) = 0$ yields

$$g_\alpha(0) = 1 \qquad \widetilde{C}_\alpha(0) = k_\alpha X_\alpha t \quad (292)$$

The solutions of the partial differential equations (Eqs (290) and (291)) with initial conditions $g^0_\alpha(p_\alpha)$ and $\widetilde{C}^0_\alpha(p_\alpha)$ are obtained by means of the method of characteristics [96]

$$g_\alpha(p_\alpha) = \frac{\tau_\alpha}{p_\alpha + \tau_\alpha} + \frac{p_\alpha}{p_\alpha + \tau_\alpha} g^0_\alpha(p_\alpha + \tau_\alpha) \quad (293)$$

$$g^h_\alpha(p_\alpha) \equiv \frac{\widetilde{C}_\alpha(p_\alpha)}{\widetilde{C}_\alpha(0)} = \frac{\tau_\alpha}{p_\alpha + \tau_\alpha} + \frac{p_\alpha\left[1 - g^0_\alpha(p_\alpha + \tau_\alpha)\right]}{\bar{l}^0_\alpha(p_\alpha + \tau_\alpha)^2} \quad (294)$$

Performing in these formulas the inverse Laplace transform will result in expressions 170 and 171 for MWDs of types 1 and 2 blocks in a copolymer and MWDs of homopolymers, respectively. The knowledge of the first two of these distributions enables, proceeding from formula A1, to find the evolution of SCD $f_{12}(l_1, l_2)$ of the block copolymer molecules during their degradation. The center $\bar{l}_\alpha$ and the dispersion $\sigma^2_\alpha = \overline{l^2_\alpha} - \bar{l}^2_\alpha$ of the distribution for length l_α of α-th type block in a copolymer are easy to find by differentiating its generating function (Eq (293)) and setting $p_\alpha = 0$

$$\bar{l}_\alpha = \frac{1 - g^0_\alpha(\tau_\alpha)}{\tau_\alpha}, \qquad \sigma^2_\alpha = \frac{1}{\tau^2_\alpha}\left\{2\tau_\alpha g^{0\prime}_\alpha(\tau_\alpha) + 1 - \left[g^0_\alpha(\tau_\alpha)\right]^2\right\} \quad (295)$$

An analogous procedure being applied to the generating function of MWD of α-th type homopolymers enables to get simple expressions for their number average degree of polymerization $P^h_{n\alpha}$ and polydispersity coefficient K^h_α

$$P^h_{n\alpha} = \frac{1}{\bar{l}^0_\alpha \tau_\alpha}\left(\bar{l}^0_\alpha - \bar{l}_\alpha\right), \quad K^h_\alpha \equiv \frac{P^h_{w\alpha}}{P^h_{n\alpha}} = \frac{2\bar{l}^0_\alpha\left[\bar{l}^0_\alpha - g^{0\prime}_\alpha(\tau_\alpha) - 2\bar{l}_\alpha\right]}{\left(\bar{l}^0_\alpha - \bar{l}_\alpha\right)^2} \quad (296)$$

Knowing the generating functions $g^0_1(p)$ and $g^0_2(p)$ of the distributions of blocks for length in the initial copolymers as well as their derivatives $g^{0\prime}_1(p)$ and $g^{0\prime}_2(p)$, it is not

a serious problem to find the explicit dependence of the statistical characteristics (Eqs (295) and (296)) of the degradation products on time.

When τ_α tends to zero in the right hand part of the first formula 296 this latter is reduced to the relationship $P^h_{n\alpha} = P_{w\alpha}/2$, connecting the average degree of polymerization of homopolymers, being formed in the very beginning of the degradation, $P^h_{n\alpha}$, with that, $P_{w\alpha}$, which the blocks used to have in initial copolymer. Performing the limit $\tau_\alpha \to 0$ in the second formula 296 results in an analogous relation $K^h_\alpha = 4K'_\alpha/3$ between the polydispersity coefficients.

The above formulas enable to make two important conclusions. Firstly, at sufficiently high polydispersity of blocklength in the initial copolymer, i.e. at $K_\alpha > 2$, their average degree of polymerization, $P_{n\alpha}$, proves to be less than the average length of homopolymers, $P^h_{n\alpha}$, formed under the degradation of these blocks. The reason for this effect is due to the fact that polymeric chains with high molecular weights are more susceptible to degradation since the constant of this molecular reaction $k_\alpha l_\alpha$ grows with the length of block l_α. The second essential conclusion consists in the answer to the question whether the MWD of homopolymers formed at the very beginning of the degradation of initial copolymer blocks is wider or narrower than the MWD of these latter. It turns out to be that the first case is realized if the ratio between polydispersity coefficients K'_α/K_α is larger than 3/4, while the second case takes place when this ratio is less than 3/4.

When interpreting data obtained by a chromatographic experiment, the expression for the distribution of block copolymer molecules for their size $l = l_1 + l_2$ regardless of their composition can be of special interest. The generating function of such a one-dimensional distribution $f^s_{12}(l)$ can be obtained from the following expression

$$g_{12}(p) \equiv \int_0^\infty f^s_{12}(l) \exp(-pl)\, dl = g_1(p)\, g_2(p) \tag{297}$$

where functions g_1 and g_2 have been determined above (Eq (293)). The n-th order statistical moment of distribution $f_{12}(l)$ is, evidently, equal up to the factor $(-1)^n$ to the derivative of the same order of the generating function $g_{12}(p)$ taken at point $p = 0$. Because the random quantities l_1 and l_2 are independent, the dispersion σ^2_α of their sum $l = l_1 + l_2$ will equal the sum of dispersions σ^2_1 and σ^2_2, where σ^2_α are defined by formula 295.